ABSTRACT

Methanol is the bulk feedstock for chemical industry and nowadays emerges as a suitable environmental friendly fuel. Conventional Lurgi Process of methanol producing from synthesis gas employs Cu/ZnO catalyst which, however, shows a steady deterioration of chemical and mechanical properties. This deterioration affects the production of methanol, especially during the third year of the catalyst operation. In this study, comparisons are made on the catalyst surface in order to determine the causes of the catalyst deterioration based on real industrial process condition between Sud Chemie's fresh commercial catalyst and the second-year in operation commercial catalyst. The operating condition of the methanol synthesis based on Lurgi technology is 250°C and 30 bar [2]. The surface morphology of the catalyst was visualized by *Field Emission Scanning Electron Microscopy/Energy Dispersive X-ray Analysis* and *X-ray Photoelectron Spectroscopy*. The information obtained from this research will be used to develop a model of poisoning catalyst deactivation.

CHAPTER 1

INTRODUCTION

1.1 Project Background

Methanol (CH_3OH) is an industrially important base chemical, which used for production of formaldehyde, methyl-tert-butyl-ether and acetic acid. Nowadays, where the oil and gas reserves diminish and the demands for energy increases, the methanol becomes one of the candidates of being used as alternative fuel. It has the attribute which exists in liquid state. This makes the methanol relevant to become fuel. Furthermore, the methanol can be formed from CO_2 which can potentially become one of good method to recycle the CO_2.

To produce the methanol, we use a heterogeneous catalyst which is the $Cu/ZnO/Al_2O_3$. This catalyst is being used with the Lurgi Methanol Reactor technology. Here, we focusing the PETRONAS Methanol Labuan Sdn. Bhd. which using this technology.

Methanol can be produced from syngas, either CO or CO_2. The syngas is obtained from the natural gas by a steam reforming process. Methane of the natural gas is mixed with steam at 3/1 ratio. It is then reformed to carbon oxides and hydrogen and reacts exothermically in the gas phase to form mainly methanol and water mixture. For this reaction, it is where the Cu, Al and Zn based catalyst plays its role.

Until year 2000, the worldwide production of methanol stands about 12.5 billion gallons (37.5 million tons) per year with rate of utilization about 80 percent. The worldwide methanol industry had given a big impact on the economy, where this industry generated $ 12 billion annually and also creating over 100000 job opportunities directly and indirectly. This shows that this industry has a bright future, where in 2008 the methanol consumption was approximately 15 billion gallons (45 million tons) which equivalent to the world demand. It is expected in 2012 the demand will reach to over 17 billion gallons. This number will grow along the production rate of methanol which also growing to 28 billion gallons (85 million metric tons).

1.2 Problem Statement

The methanol production plant at Methanol Labuan Sdn. Bhd. using catalyst $Cu/ZnO/Al_2O_3$. The life of this catalyst is about 3 years before it will be poisoned and the effectiveness of the catalyst is not at the optimum condition. As a result, the production rate of methanol during the 3rd year of the catalyst being put into service decreased up to 3rd year of service.

One of the reasons why the catalyst loses its ability to speed up the reaction is the transformation of the surface of the catalyst itself. The transformation could be in the form of sintering of the catalyst which make the surface area of the catalyst become smaller.

Therefore, there is a suggestion to lengthen the life spent of the catalyst to 6 years in order to cut the cost of buying the supply of the catalyst.

1.3 Research Objectives

The objective of this research is to investigate the surface transformation of $Cu/ZnO/Al_2O_3$ catalyst on the methanol production per annum by using Lurgi methanol production. This research involves observing the sample of industrial catalyst which obtained from PETRONAS Methanol Labuan Sdn. Bhd. (PML) which consist of :

- Fresh catalyst
- 2 years in service
- 3 years in service

The goal of this research are :

1. To initially conduct a characterization of the spent catalyst obtained from PMLSB (2 years of operation)
2. To compare the surface features of fresh commercial catalyst and spent catalyst after two and three years of industrial operation.
3. To give an insight into the process of catalyst deactivation

Therefore using those samples, we can analyze the real cause and impact of the catalyst surface transformation. The study will be done by the following analytical methods

1. FESEM : Field Emission Scanning Electron Microscopy
2. EDX mapping : Energy Dispersive X-Ray Analysis
3. XPS : X-Ray Photoelectron Spectroscopy

1.4 Scope Of Study

The study is divided into 4 parts :

1. The literature review

   To conduct literature review on the $Cu/ZnO/Al_2O_3$ catalyst. This scope covers the preliminary research on potential causes of catalyst deactivations

2. Analysis of Samples

   The samples obtained from PMLSB to be studied by:

   - Field Emission Electron Microscopy (FESEM)
   - Energy Dispersive X-Ray Elemental Analysis
   - X-ray Photoelectron Spectroscopy (XPS)

3. Result Analysis

   Results obtained from the laboratory tests will be analyzed and interpreted. The result is important in order to achieve all the objective of the project. Alterations of surface morphology and chemical composition of the fresh and spent catalysts to be compared and analysed.

4. Catalyst Aging Model Development

   The model is developed based on the literature review and comparison results

CHAPTER 2

LITERATURE REVIEW

2.1 Methanol Production

Methane is often used as the feedstock to produce methanol, where the methane is reacted with a high pressure steam and at high temperature. This process will produce synthesis gas of low methane content. Most of the carbon will be converted to CO and CO_2.

$$CH_4 + H_2O \xrightarrow[1000\ DC]{} CO + 3H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

Mixture of hydrogen and carbon oxides compressed and passed over a catalyst under high pressure and temperature. Thus the methanol is formed.

$$CO + 2H_2 \xrightarrow[400\ DC]{} CH_3OH$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

The mixture of methanol, water and other impurities will undergo distillation process to recover about 99.95 mole percent purity. [5]

In industrial process, conversion of natural gas to synthesis gas to produce methanol is widely used. To produce syngas, steam reforming of the natural gas must be done. Nowadays, the steam reforming process consists of two-step reforming; primary steam reforming and autothermal reforming. The function of primary reformer is to produce CO and H_2O with heat generation. Meanwhile, for the secondary reformer, it held the same function but operated in higher temperatures to ensure low leakage of methane.

2.1.1 Lurgi Methanol Production

This process is an advanced technology for converting natural gas to methanol at low cost in large quantities. The main features of this process are :

1. Oxygen-blown natural gas reforming, either in combination with steam reforming, or as pure autothermal reforming.

2. Two-step methanol synthesis in water and gas cooled reactors operating along the optimum reaction route.

3. Adjustment of syngas composition by hydrogen recycle.

2.1.2 Synthesis Gas Production

This section accounts for more than 50% of the capital cost of a methanol plant. Thus, the optimization of this section yield a significant cost benefit.

Conventional steam reforming is economically applied in small and medium-sized methanol plants, with the maximum single-train capacity being limited to 3000 mtpd. The technology of oxygen-blown natural gas reforming, whether in combination with steam reforming or as pure auto thermal reforming, considered to be the best for syngas plants.

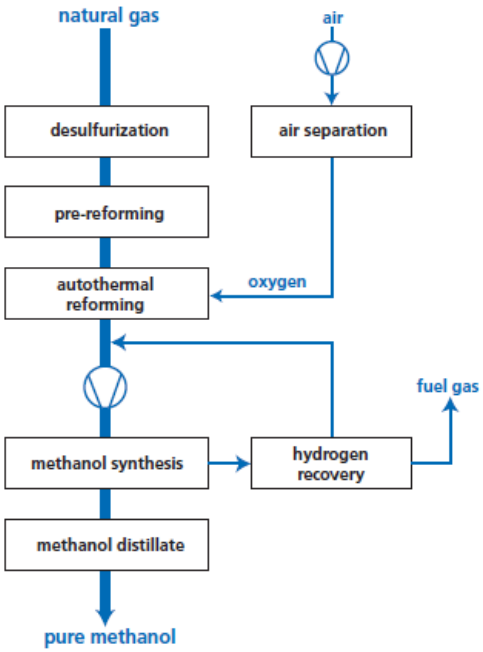


Figure 1 : Methanol Production using Lurgi Autothermal Reforming

This system is applicable for the feed which is the light natural gas as the feedstock. The optionally pre reformed and desulfurised feed is reformed with steam to synthesis gas at about 40 bar and higher using oxygen as reforming agent. As a result a carbon-free synthesis

gas generated. The outlet temperature of the reformer normally 950 – 1050 DC. The synthesis gas is later compressed in a single casing synthesis gas compressor with integrated recycle stage to the pressure which is required for the system to synthesis the methanol.

As we know, this system is suitable to process the light natural gas. Therefore, even if using the pure methane as the feedstock for the autothermal reforming, it is necessary to condition the synthesis gas, as its stoichiometric number is below 2.0. The most economic to achieve the required gas composition is to add hydrogen which withdrawn from the methanol synthesis purge stream through by a membrane unit or a pressure adsorption unit.

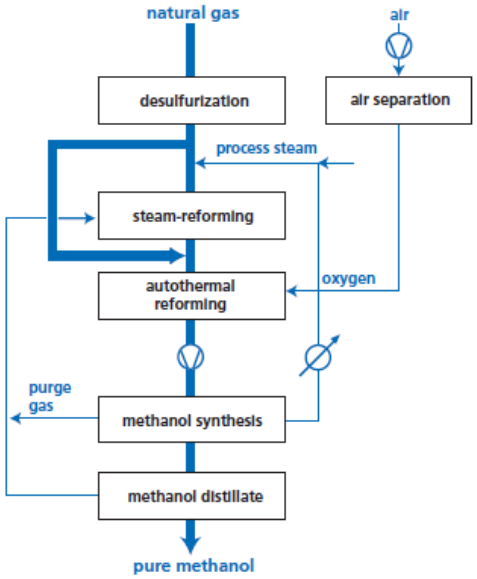


Figure 2 : Methanol Reforming using Lurgi Combined Reforming

This kind of process is for the required for the heavy natural gases and oil-associated gases. This is because, if we use the autothermal reforming, the required stoichiometric number cannot be obtained by pure autothermal reforming even if all hydrogen available is recycled. For these applications, the Lurgi Methanol production process concept combines autothermal and steam reforming as the most economic way to generate synthesis gas for methanol plants. After desulfurization, a feed gas branch stream is decomposed in a stream reformer at high pressure (35-40 bar) and lower temperature than the previous process (700 – 800 DC). The reformed gas in then mixed with the remainder of the feedgas and reformed to syngas at high pressure in the autothermal reactor.

2.1.3 Lurgi MegaMethanol Process

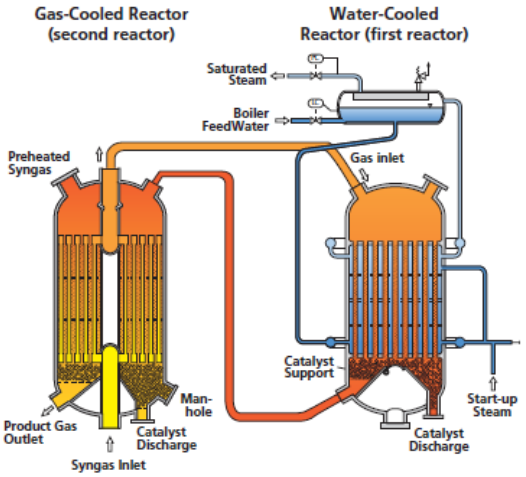


Figure 3 : Lurgi MegaMethanol Process

Low cost methanol production can be achieved by an efficient syngas-to-methanol conversion. Also, the optimum utilization of reaction heat offers cost advantage and energy savings for the overall plant. Therefore, Lurgi equipped its methanol plants with tubular reactor which transfers the heat of reaction to boiling water.

The Lurgi Methanol Reactor is basically a vertical shell and tube heat exchanger with fixed tube sheets. The catalyst is accommodated in tubes and rests on a bed of inert material. The water/steam mixture generated by the heat of reaction is drawn off below the upper tube sheet. Steam pressure control permits exact control of the reaction temperature. This isothermal reactor achieves very high yields at low recycle ratios and minimizes the production of by-products. Based on the Lurgi Methanol Reactor and the highly active methanol catalyst with its capability to operate at high space velocities, Lurgi has recently developed a dual reactor system featuring higher efficiency. The isothermal reactor is combined in series with a gas-cooled reactor.

The first reactor, the isothermal reactor, accomplishes partial conversion of the syngas to methanol at higher space velocities and higher temperatures compared with single stage synthesis reactors. This results in a significant size reduction of the water-cooled reactor compared to conventional processes, while the steam raised is available at a higher pressure. The methanol-containing gas leaving the first reactor is routed to a second downstream

reactor without prior cooling. In this reactor, cold feedgas for the first reactor is routed through tubes in a countercurrent flow with the reacting gas.

Thus, the reaction temperature is continuously reduced over the reaction path in the second reactor, and the equilibrium driving force for methanol synthesis maintained over the entire catalyst bed. The large inlet gas preheater normally required for synthesis by a single water-cooled reactor is replaced by a relatively small trim preheater.

As fresh synthesis gas is only fed to the first reactor, no catalyst poisons reach the second reactor. The poison-free operation and the low operating temperature result in a virtually unlimited catalyst service life for the gas-cooled reactor.

In addition, reaction control also prolongs the service life of the catalyst in the water-cooled reactor. If the methanol yield in the water-cooled reactor decreases as a result of declining catalyst activity, the temperature in the inlet section of the gas-cooled reactor will rise with a resulting improvement in the reaction kinetics and, hence, an increased yield in the second reactor.

After cooling and separation of the purge gas, the crude methanol is processed in the distillation unit. In the hydrogen recovery unit, H2 is separated from the purge gas and recycled to the syngas loop. The remaining CH4-rich gas fraction is used as fuel gas.

The most important advantages of the Combined Synthesis Converters are:

- High syngas conversion efficiency. At the same conversion efficiency, the recycle ratio is about half of
  the ratio in a single-stage, water-cooled reactor.
- High energy efficiency. About 0.8 t of 50–60 bar steam per ton of methanol can be generated in the reactor. In addition, a substantial part of the sensible heat can be recovered at the gas-cooled reactor outlet.
- Low investment cost. The reduction in the catalyst volume for the water-cooled reactor, the omission of the large feedgas preheater and savings resulting from other

equipment due to the lower recycle ratio translate into specific cost savings of about 40% for the synthesis loop.

- High single-train capacity. Single-train plants with capacities of 5000 mt/day and above can be built.

2.1.4 Methanol Distillation

The crude methanol is purified in an energy-saving 3-column distillation unit. With the 3-column arrangement, the low boilers are removed in the pre-run column and the higher boiling components are separated in two pure methanol columns. The first pure methanol column operates at elevated pressure and the second column at atmospheric pressure. The overhead vapours of the pressurised column heat the sump of the atmospheric column. Thus, about 40% of the heating steam and, in turn, about 40% of the cooling capacity are saved. The split of the refining column into two columns allows for very high single-train capacities.

2.2 Catalyst $Cu/ZnO/Al_2O_3$

$Cu/ZnO/Al_2O_3$ catalyst represents a versatile catalyst system for methanol chemistry, especially in the synthesis of methanol process. Most of the $Cu/ZnO/Al_2O_3$ catalyst is prepared with a fixed composition of Cu/Zn/Al = 60:30:10 which were investigated by *in situ* bulk techniques, X-ray diffraction, and X-ray absorption spectroscopy.[7] This catalyst's microscopic and morphological structural characteristics is examined by electron microscopy (TEM). On this section, the overview of $Cu/ZnO/Al_2O_3$ preparation and deactivation will be discussed.

2.2.1 Process of $Cu/ZnO/Al_2O_3$ Preparation

The preparation of $Cu/ZnO/Al_2O_3$ by using novel oxalate gel coprecipitation is one of the popular method in methanol synthesis industry. This is because this method has proven to produce a large specific surface area, highly dispersion ultrafine $Cu/ZnO/Al_2O_3$ catalysts, which exhibited a higher catalytic activity and optimum methanol selectivity for methanol synthesis from CO/CO_2. In journal "Study of Effect of Preparation Method of $Cu/ZnO/Al_2O_3$" by Wensheng Nen, Hangyan Shen and Huazhang Liu stated that; "The catalyst prepared by oxalate gel coprecipitation showed higher BET area and smaller particle size than those by the other methods, and it also showed the highest activity and methanol selectivity"[6].

The catalyst was prepared with an oxalate gel-coprecipitation method. The typical procedure to prepare the catalyst is by mixing oxalic acid and mixed salts of copper nitrate, zinc nitrate and aluminium nitrate. The molar ratio of the components in the nitrates, Cu, Zn and Al is 6 : 3 : 1. The mixture of oxalic acid and the nitrates are dissolved in ethanol, respectively. The solution of oxalic acid and ethanol is rapidly added to the mixed solution of metal nitrates at 25 C under vigorous stirring until a gel-like precipitate was formed. This precipitate is later separated by centrifuge [6,7].

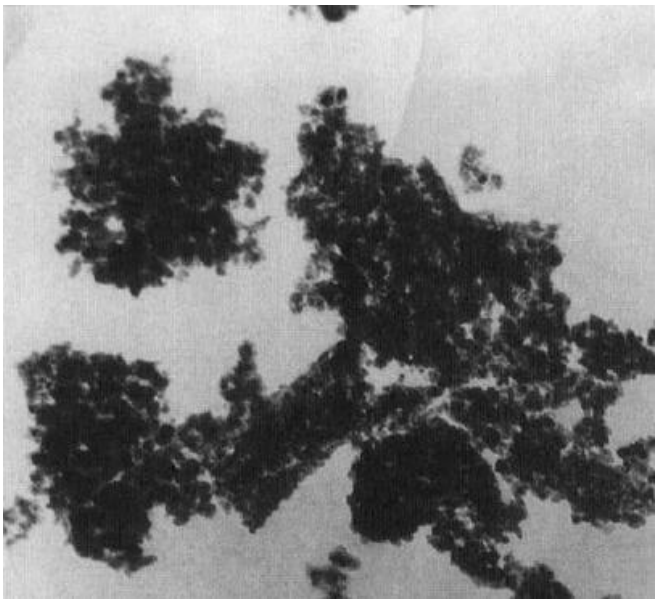


Figure 4 : TEM micrographs of CZA catalyst

It is well known that the Cu is essential part of the catalyst which act as active site for the reaction of methanol synthesis. Studies have proven that for a given type of catalyst and a given synthesis gas composition, the methanol formation rate is directly proportional to the metallic copper area [8]. Thus, it is believed that a higher metallic copper area (finer particle size of metal copper) results in a higher activity for $Cu/ZnO/Al_2O_3$ catalyst [6]. The finer the particle size of the catalyst, the dispersion of Cu at the catalyst itself will be better. Thus, more surface area of the catalyst will be exposed to the process.

2.2.2 Deactivation of $Cu/ZnO/Al_2O_3$

As mentioned in the title, we are studying the impact of gradual chemical transformation on the catalyst's surface. The transformation of the catalyst can lead to its loss of effectiveness, where the production of the methanol in PML declines during the 3rd year of

service of the catalyst. Especially from the industrial viewpoint, the fundamental research of $Cu/ZnO/Al_2O_3$ catalysts is not only related to activity and selectivity but also to the catalyst stability, chemical and thermal durability, and poison resistance. Cu has a low *Tammann* temperature corresponding to a low melting point of 1080 °C. Therefore, this catalyst has high tendency to suffer from thermal deactivation by sintering at temperatures above 300 °C [7, 9]. Thermal stability of copper based catalysts strongly depends on both the preparation procedures used and the chemical composition. Hence, the catalyst preparation is a crucial point in order to prepare the catalyst for the effect of post reaction toward its surface and its effectiveness [6]. Principally, deactivation of Cu based catalysts are caused by sintering of copper crystallites, poisoning by impurities, and poisoning and blockage by high hydrocarbon by-products.

Operating catalysts at low temperature thermodynamically favors adsorption of poisons, giving high surface coverage. As a result, copper catalysts are extremely sensitive to site-blocking poisons, and they are particularly sensitive to even very low levels of poison such as reduced sulphur or phosphorus species [4]. Under normal operating conditions sulphur is a powerful poison for copper. Therefore, it is safe to state that, the desulfurization of the natural gas as the feedstock to produce syngas is a must, as stated by Martyn V. Twigg and Michael S. Spencer "If present in the reactant feed, sulphur from H2S or other sulphur compounds accumulates on copper catalysts, and it is therefore important to eliminate sources of sulphur contamination during use. It was for these reasons that the introduction of copper catalysts for methanol synthesis was delayed until sufficiently pure synthesis gas became available" [4].

The catalyst $Cu/ZnO/Al_2O_3$ are very susceptible toward the poisoning of the impurities. The impurities in the feed come in the form of chemically bonded compound. For example, H_2S, tiophene and COS. The sulphur come from residual sulphur which resides in coal which burned in order to get synthesis gas. Therefore, in order to protect the Cu surface from being poisoned, the catalyst is made consists of ZnO. In these catalysts the small crystallite size of ZnO, coming from the method of manufacture, ensures that the kinetics of reactive absorption are very fast. From the Handbook of Commercial Catalyst, page 432, written by Howard F. Rase, is states that "ZnO reacts readily with copper poisons such as sulphur and chlorine compounds" [1]. In our case, the sulphur potentially exists in the feed in

the form of hydrogen sulphide, H_2S. ZnO is very effective in limiting poisoning by the removal of H_2S from gas steams with the formation of zinc sulphur. Indeed, it is used in industrial applications for sulphur removal from natural gas. The efficiency of this reaction in preventing poisoning has been confirmed by equilibrium calculations from M.S. Spencer, Topics Catal. 8 (1999). The absorption reaction is shown in equation [9]:

$$ZnO\ (s) + H_2S\ (g) \rightarrow ZnS\ (s) + H_2O\ (g)$$

To retain the long-term activity of Cu catalysts it has been empirically found that gas phase sulphur concentrations need to be kept below 1 ppm and preferably below 0.1 ppm.

Another mode of the catalyst deactivation is the thermal sintering. Sintering is the bonding together of compacted particles at temperatures below the melting point of the particular metal. This bonding produces larger forms of crystallites which take place at the catalyst's active site. That is why the Cu based catalysts shows deactivation symptoms even there are no impurities like sulfur and chlorine in the system to poison the catalyst [3, 9]. Therefore, when part of the active site have occupied, this reduces the amount of catalytic surface area. For metals, the predominant sintering mechanism in the bulk is vacancy diffusion which suggests a relationship with cohesive energy. Hughes, in his writing, *Deactivation of Catalysts* gave the following increasing order of stability for metals: Ag < Cu < Au < Pd < Fe < Ni < Co < Pt < Rh < Ru < Ir < Os < Re: It is therefore not surprising that copper-based catalysts are more susceptible to thermal sintering than other commonly used metallic catalysts, such as the nickel, iron, palladium and platinum catalysts used in many hydrogen and dehydrogenation reactions [4]. This is also shown by M.S. Spencer, which reflects a relatively low melting point (1063 C), compared with, for example, that of iron (1535 C) and nickel (1455 C). Therefore, copper-based catalysts have to be operated at relatively low temperatures, usually no higher than 300 C.

Other than that, the sintering processes at high temperatures are also affected by atmosphere. Supported metal catalysts sinter relatively rapidly under an oxidizing atmosphere, however the process is more slow under reducing and inert atmospheres, as stated from Wanke & Flynn 1975. Sintering is also generally accelerated by the presence of water vapour, as stated of Mowery *et al.* 1999, Bartholomew 2001. For our case here, the water vapour is

produced as byproduct from 2 reactions, as taken from James T. Sun, Ian S. Metcalfe and Mortaza Sahibzada in their journal, *Deactivation of Cu/ZnO/Al_2O_3 Methanol Synthesis Catalyst by Sintering* :

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

$$CO_2 + H_2 \rightarrow CO + H_2O$$

Which could lead to severe sintering effect of the Cu/ZnO/Al_2O_3 surface.

Here, we are using the oxides support in order to minimize the sintering effect. Therefore, the oxide support such as Al_2O_3 plays its role by separating the Cu particles from being concentrated only at one point in order to prevent them to agglomerate. Thus, industrially employed Cu/ZnO catalysts for methanol chemistry contain additional refractory phases, such as Al_2O_3 to minimize thermal sintering. However, it is desirable to minimise the amount of stabiliser, because if it has negligible activity itself it dilutes the effective catalyst component. Although ZnO has some activity for methanol synthesis, this is much less than that of Cu and it is effectively an inert diluent.

In journal "Deactivation of Supported Copper Catalyst for Methanol Synthesis" by M. Kurtz et. al., an experiment was conducted in order to investigate the effect of methanol synthesis process on the Cu surface and also to investigate the function of the supported metal (ZnO and Al_2O_3) toward reducing Cu/ZnO/Al_2O_3 deactivation time [9].

In this experiment, 3 specimens are being investigated :

- Cu/ZnO (Al_2O_3 free)
- Cu/Al_2O_3 (ZnO free)
- Cu/ZnO/Al_2O_3

The experiment is conducted in condition of :

- T = 473 K
- P = 0.1 MPa

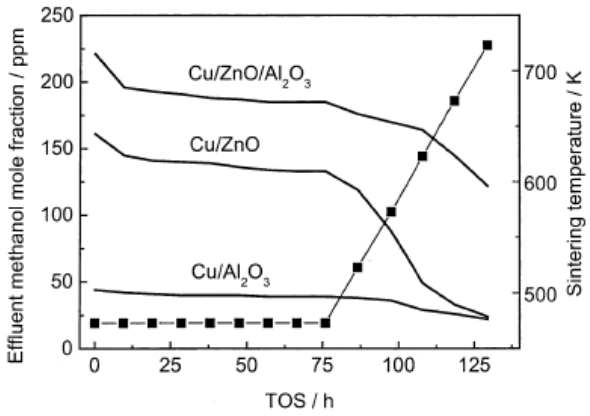


Figure 5 : Effluent Methanol Mole Fraction versus Time of Stream (TOS) versus Sintering Temperature Graph

Based on the result which shown above, we can see the activity of the respective catalyst, where the $Cu/ZnO/Al_2O_3$ is the highest activity, followed by the Cu/ZnO. The Cu/Al_2O_3 shows the poorest activity. The activity of Cu/Al_2O_3 is the lowest because the Al_2O_3 functions as a support to reduce the sintering effect. Therefore, that's why the this catalyst shows a steady behaviour on the deactivation during the increment of sintering effect. On the other hand, as for Cu/ZnO, the initial activity of this catalyst higher than Cu/Al_2O_3, but the deactivation rate due to the sintering temperature increment. This because, apart from being the protector to prevent poisoning to the Cu, ZnO also act as active catalyst toward the methanol synthesis as stated in dissertation "A Comparative Study of Spent Industrial $Cu/ZnO/Al_2O_3$ Catalyst for Methanol Synthesis and In-House Made Catalysts Promoted With Carbon Nanotubes" by Saidolim Saidakrorov [2]. Based on this statement and also the result of the experiment, both support metal are needed in order to make sure the catalyst is in high activity and also to reduce effect of sintering.

Another issue on the catalyst deactivation is the impurities which exists on the catalyst itself. For example, there are impurities such as K^+ and Cs^+ on the surface of the catalyst which has the potential to produce higher hydrocarbon [7, 13]. Those higher hydrocarbons are thermodynamically favoured byproducts during hydrogenation of CO/CO_2 in methanol synthesis process. These hydrocarbon will destroy the active sites on the catalyst by depositing on the surface of the catalyst. Therefore, the pore which contain the active sites will be blocked and this phenomenon will decrease the effectiveness of the catalyst.

CHAPTER 3

METHODOLOGY

3.1 Overview of Methodology

The following is the summary of procedures involved for this project in chronological order.

1. The spent commercial catalyst which being used by PMLSB for methanol synthesis being discharged from the reactor after 2 years of operation was obtained.
2. Information needed for the model development being discussed and determined. The needed information :
    - The changes of composition surface
    - Dispersion of Cu and ZnO
    - Contamination on the surface
3. The surface morphology of the spent commercial catalyst samples were investigated using suitable analytical methods :
    - FESEM : Create imaging on the sample surface to visualize the surface morphology
    - EDX : To create mapping of the elements to observe their dispersions
    - XPS : To detect chemical compound and contaminant which existed on the catalyst surface
4. The surface characteristics obtained from the spent commercial catalyst analysis were compared with surface characteristics of fresh commercial catalyst and 3-years spent catalyst. The target is to reveal irregularities of reaction conditions in the reactor.
5. Developing catalyst deactivation by using information obtained by samples analysis and literature review.

3.2 Equipments for Sample Analysis

3.2.1 Field Emission Scanning Electron Microscopy (FESEM)

FESEM is an electron microscope which provides high resolution images of a specimen which has the resolution up to 10 nm. The working principle of the instrument is, a field-emission cathode in the electron gun of a scanning electron microscope provides narrower probing beams at low as well as high electronenergy, resulting in both improved spatial resolution and minimized sample charging and damage. The ejected electron field of FESEM is also focused not by a magnetic but an electronic lense. It gives much higher resolution than the conventional SEM and gives better imaging of trenches and deep holes.

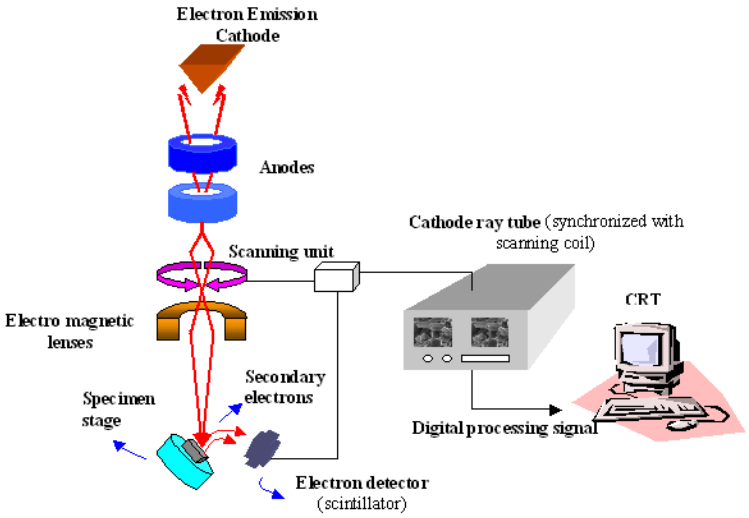


Figure 6 : FESEM Image Generation Sequence

The ejected beam from the electron emission cathode is shoot toward the surface of the sample which needs investigating. Those electrons which bombarded will be backscattered and they are used to determine the composite material of the surface. Meanwhile, there are secondary electrons which ejected from the sample itself is detected by the electron detector. Thus, an image of the sample surface is constructed by comparing the intensity of these secondary electrons to the scanning primary electron beam. Finally the image is displayed on a monitor.

3.2.2 Energy Dispersive X-ray analysis (EDX)

As for the EDX mapping, it is a technology where the user can determine the element which occupies the surface area of the catalyst. EDX Analysis stands for Energy Dispersive X-ray analysis. It is sometimes referred to also as EDS or EDAX analysis. It is a technique used for identifying the elemental composition of the specimen, or an area of interest thereof. The EDX analysis system works as an integrated feature of a scanning electron microscope (SEM), and cannot operate on its own without the latter.

During EDX Analysis, the specimen is bombarded with an electron beam inside the scanning electron microscope. The bombarding electrons collide with the specimen atoms' own electrons, knocking some of them off in the process. A position vacated by an ejected inner shell electron is eventually occupied by a higher-energy electron from an outer shell. To be able to do so, however, the transferring outer electron must give up some of its energy by emitting an X-ray.

The amount of energy released by the transferring electron depends on which shell it is transferring from, as well as which shell it is transferring to. Furthermore, the atom of every element releases X-rays with unique amounts of energy during the transferring process. Thus, by measuring the amounts of energy present in the X-rays being released by a specimen during electron beam bombardment, the identity of the atom from which the X-ray was emitted can be established.

The output of an EDX analysis is an EDX spectrum. EDX spectrum is just a plot of how frequently an X-ray is received for each energy level. An EDX spectrum normally displays peaks corresponding to theenergy levels for which the most X-rays had been received. Each of these peaks are unique to an atom, and therefore corresponds to a single element. The higher a peak in a spectrum, the more concentrated the element is in the specimen. An EDX spectrum plot not only identifies the element corresponding to each of its peaks, but the type of X-ray to which it corresponds as well.

3.2.3 X-ray Photoelectron Spectroscopy (XPS)

The XPS that we use in this project is the JEOL JPS-9200 High Resolution X-ray Photoelectron Spectroscopy model, which used for microarea analysis and macroarea chemical state imaging on surface. The standard feature of this instrument which allows the top surface layer analysis with detection limit $1x10^{11}$ atoms/cm^2 or less.

Figure 7 : JEOL JPS-9200 High Resolution X-ray Photoelectron Spectroscopy

The concept of XPS is to describe the ejection of electrons from a surface when photons were impinged upon it. The electrons which surround the nucleus of surface atoms have their unique occupying orbitals at different energies. When the surface is radiated with X-rays from a photon source, the electrons of the surface atoms forced to be ejected, producing photoelectrons. Therefore, in order to identify surface condition based on the photoelectron emission, an analyser from the XPS measures the kinetic energy (KE). From this information, the binding energy (BE) is calculated by :

$$BE = hv - KE$$

The Binding Energy (BE) is characteristic of the core electrons for each element. The BE is determined by the attraction of the electrons to the nucleus. If an electron with energy "x" is pulled away from the nucleus, the attraction between the electron and the nucleus decreases and the BE decreases. Eventually, there will be a point when the electron will be free of the nucleus.

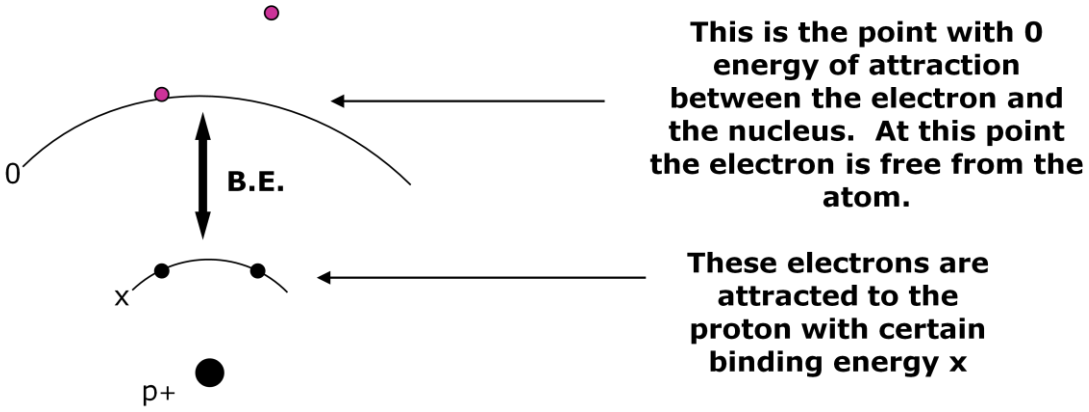


Figure 8 : Core electrons binding energy diagram

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Catalyst General Properties

In this study, we are comparing the surface properties between Sud Chemie's fresh commercial catalyst and spent commercial catalyst. Generally, by previous EDX study, the composition in weight percent of fresh catalyst is Cu (62.7 ± 7.2)%, Zn (26.7 ± 4.2)% and Al (10.6 ± 4.5)%. Based N_2O frontal chromatography analysis by Patrick Kurr et al [19], the Cu surface area is 17.5 $m^2.g^{-1}$. The surface area plays an important role as the catalytic activity depends on it.

Figure 9 : Sud Chemie Methanol Synthesis Catalyst

Figure 9 shows the field transmission electron micrographs of $Cu/ZnO/Al_2O_3$ surface where the surface is found in amorphous phase. The Cu particles are usually takes place in various morphologies such as round and irregular shapes (plates and needles).

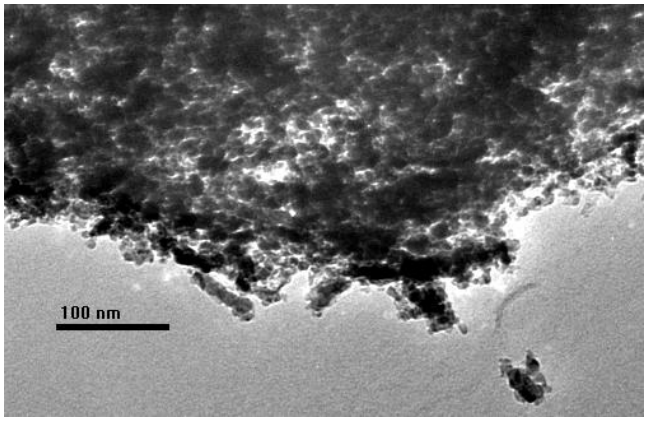


Figure 10 : SEM image of Commercial Pre-Catalyst

In Figure 10, majority of Cu particles are observed to take form in round-shape, while covered with smaller ZnO particles. Furthermore, they also homogenous small sized and well distributed. These criteria promote the effectiveness of the catalyst in the operation.

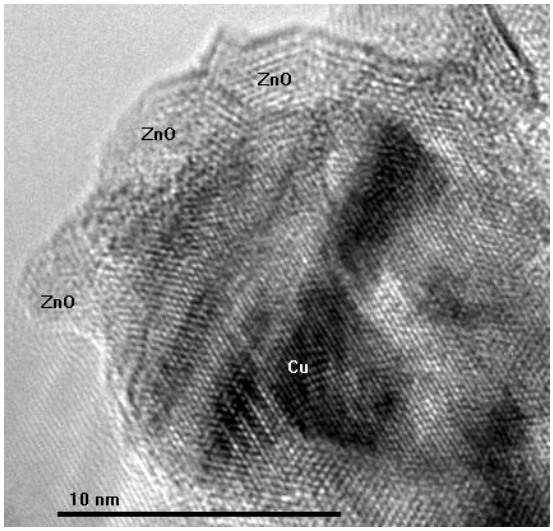


Figure 11 : TEM image of Commercial Pre-Catalyst

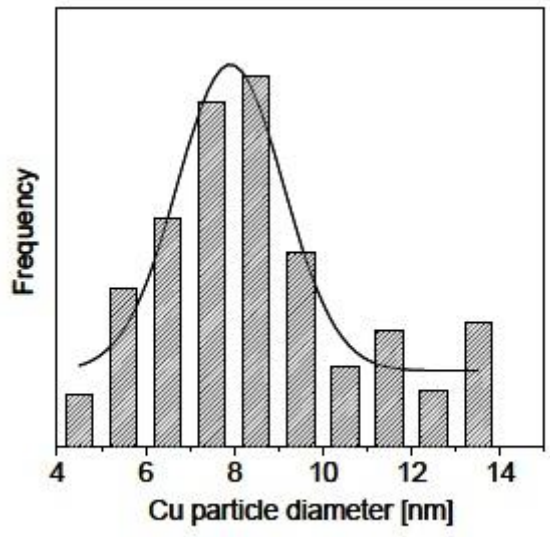


Figure 12 : Distribution of copper based on particle diameter on commercial pre-catalyst

4.1.1 Microstructure of copper (Cu)

Many references and journals stated that the activity of methanol synthesis depends on copper surface area. However, this theory is still in debut because there are findings that different from this theory. For example, Fujitani et. al confirmed that copper is not only the main factor for the activity promotional effect. They found that Zinc (Zn) contained catalyst can enhance the activity because Zn existence creates Cu-Zn active site on Cu surface. The active site was then proved by surface science study using Zn-deposited Cu(111) model [18].

However, based on Patrick Kurr et. al. findings, the derivation of bulk copper surface from its ideal structure is also important in attaining an improved catalytic performance in Zn-contained catalyst. This is because the high degree disorder in copper crystalline may result in increasing the interface area between Copper and ZnO [19]. The scattering and dispersed copper increases the copper surface area, thus increasing the catalytic activity.

The study on spent catalyst shows that the copper particles agglomerated. This condition indicates sintering of the copper particles and this leads to catalyst deactivation, where the accessible copper surface area reduced for the hydrogenation of CO_2 process to occur

4.2 Catalyst Physic-Chemical Properties

4.2.1 Density of Catalysts

Density of the catalyst is an important characteristic to determine the space which will be occupied by the catalyst inside a reactor. From this data, a suitable reactor volume which should be designed can be estimated as it can influence the amount of yield that we want to produce in the methanol plant.

Density is measured for the samples of the catalyst. The main focus is to study the changes on the spent catalyst. The fresh catalyst is used in order to make comparison of the surface changes. The data of density are obtained from Saidolim's et al [ ] studies, which the density of catalyst samples were measured by using Quantachrome Ultrapycnometer 1000 instrument. The density was measured 3 times with different samples group to reduce errors. The average value of the density was calculated and taken as the density of the sample. Lastly, the standard deviation was calculated to measure the differences of density between the samples group. The data are tabulated in Table 1.

Catalyst Sample	**Run**	**Density, ρ (g/cm^3)**	**Average Density, ρA (g/cm^3)**	**Standard Deviation (g/cm^3)**
Fresh Catalyst (0 Years)	P_1	7.32	7.31	0.02
	P_2	7.32		
	P_3	7.28		
Spent Catalyst (2 Years)	P_1	4.73	4.72	0.01
	P_2	4.73		
	P_3	4.71		

Table 1 : Densitiy of Commercial Catalyst Samples

From the tabulated data, we can see that the spent catalyst has lower density which is 4.72 g/cm^3, compared to the fresh catalyst. This is because the surface changes influenced the content of the catalyst surface. For example, based on the FESEM EDX analysis, the surface of the spent catalyst contains graphitic carbon which inserted to the catalyst as a binding agent during pelletizing process and also from the Bourdouard process [3].

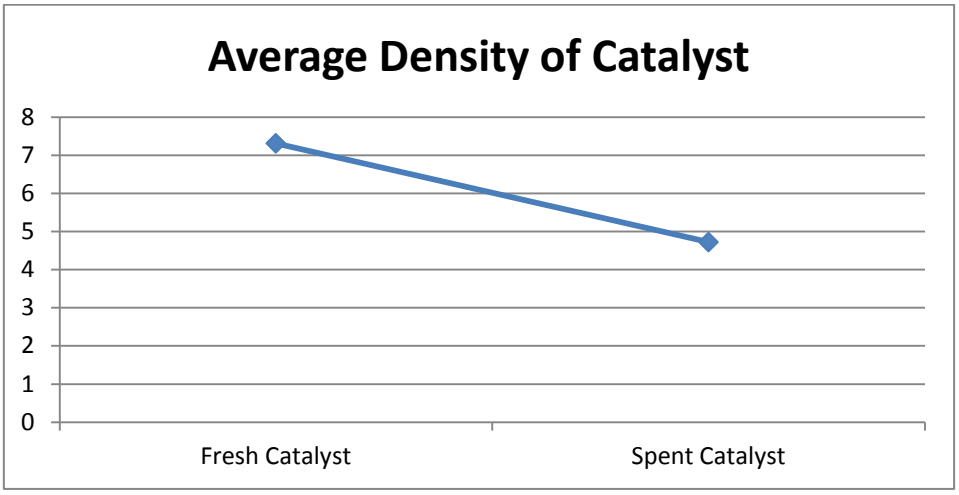


Figure 13 : Graph of Average Density of Commercial Catalyst Samples

4.3 Catalyst Structure and Morphology

4.3.1 Surface Chemistry by X-Ray Photoelectron Spectroscopy (XPS)

The surface chemistry of the sample were tested by using X-Ray Photoelectron Spectroscopy (XPS) in order to determine the exact chemical compositions that take place on the catalyst surface which had been used. The samples that were tested consist of spent catalyst samples from Reactor A and Reactor B of PML syngas to methanol conversion reactor. The Figure 14 shows the result which obtained from analysis by using Photoelectron Spectrometer JPS 9200. The JPS 9200 is equipped with differential pumping ion gun that allows elemental surface profile analysis.

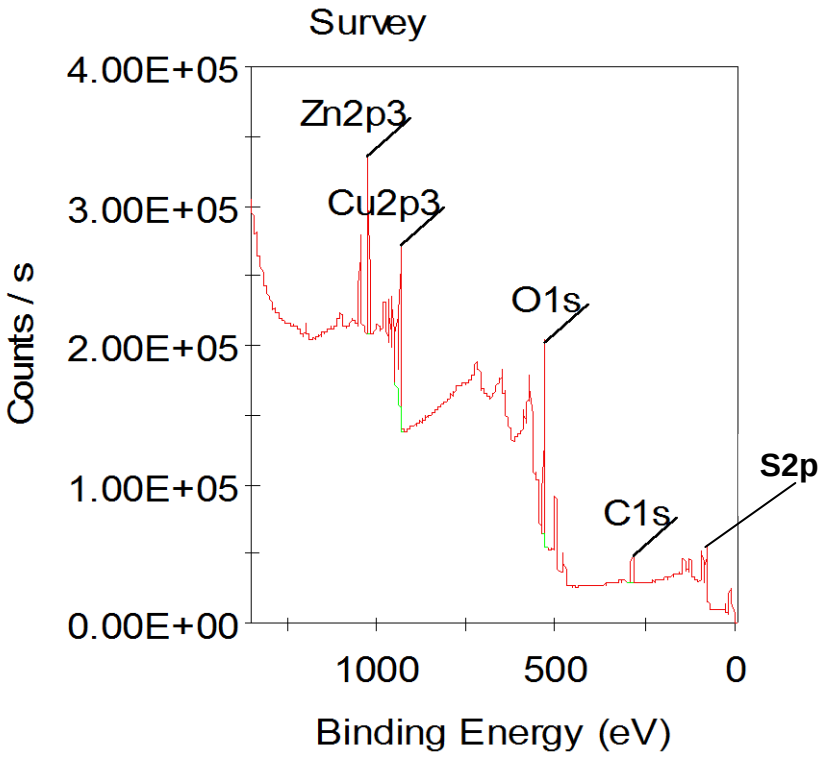


Figure 14 : Chemical States of Elements on the 2-years Spent Catalyst

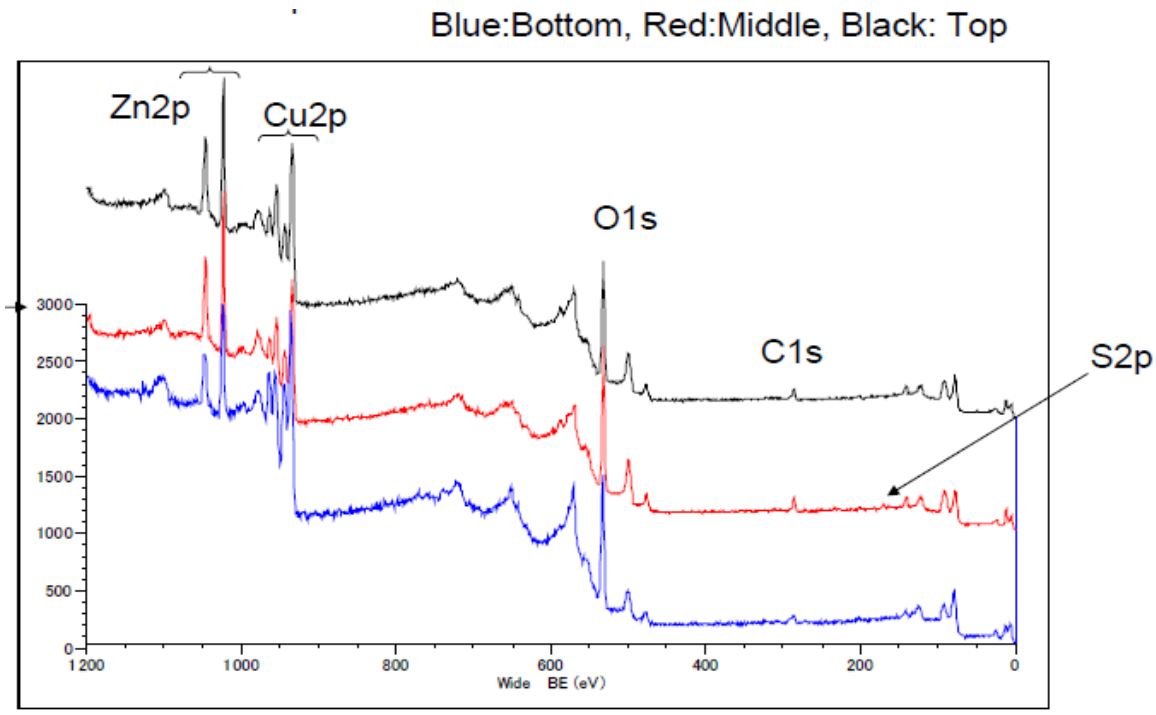


Figure 15 : Chemical States of Elements on the 3-years Spent Catalyst

The samples were not specially treated before analysis in order to retain the exact composition of the surface in condition where they were operated in the reactor. They were just degassed in the preparation chamber at high vacuum (~10^{-7} torr) about 20 minutes then transferred to the ultrahigh vacuum analytical chamber (~10^{-9} torr). The spectra of the untreated surface were recorded first, then the surface material in analytical microarea was sputtered down till 500 nm and next down till 1000 nm. The monochromatic X-ray used in this analysis and spectra were taken in high energy resolution mode.

As shown above, the S2p detected with binding energy of 161.5 eV where it takes place as ZnS. According to the literature review from M.S Spencer et. al [4], one of ZnO function reacts readily with sulfur compound in order to prevent it from poisoning the copper surface. However, ZnO also needed to enhance the activity by forming the Cu-Zn active site. Furthermore, even at very low concentrations of sulphur, due to strong metal-S bonds, sulphur chemisorbs onto the surface and reacts with the active catalyst sites, preventing reactant access. [22]

4.3.2 Surface Imaging Using FESEM

The surface is obtained by using the Field Emission Scanning Electron Microscopy (FESEM). This is a technology where the image of the surface of a solid sample is captured to determine the distribution of the elements on its surface. In this project, we are using the SUPRA 55VP by Carl Zeiss FESEM model. The samples that we used for the imaging are from Lurgi Reactor A and also from Lurgi Reactor B from PML. The images are captured by using the magnification in range of 100X to 1000X. The commercial fresh catalyst image is shown in Figure 16 with magnification 100X [2], while the spent catalyst images are shown in Figure 17 - 21

The fresh catalyst is activated by reducing the catalyst surface with 5% H_2 in N_2 gas stream at a flow rate of 76.5 ml/min from room temperature to the sample reduction temperature with ramp rate of 10°C/min. The reduction process by using hydrogen makes the copper oxide in the catalyst to produce heat and water. [25]

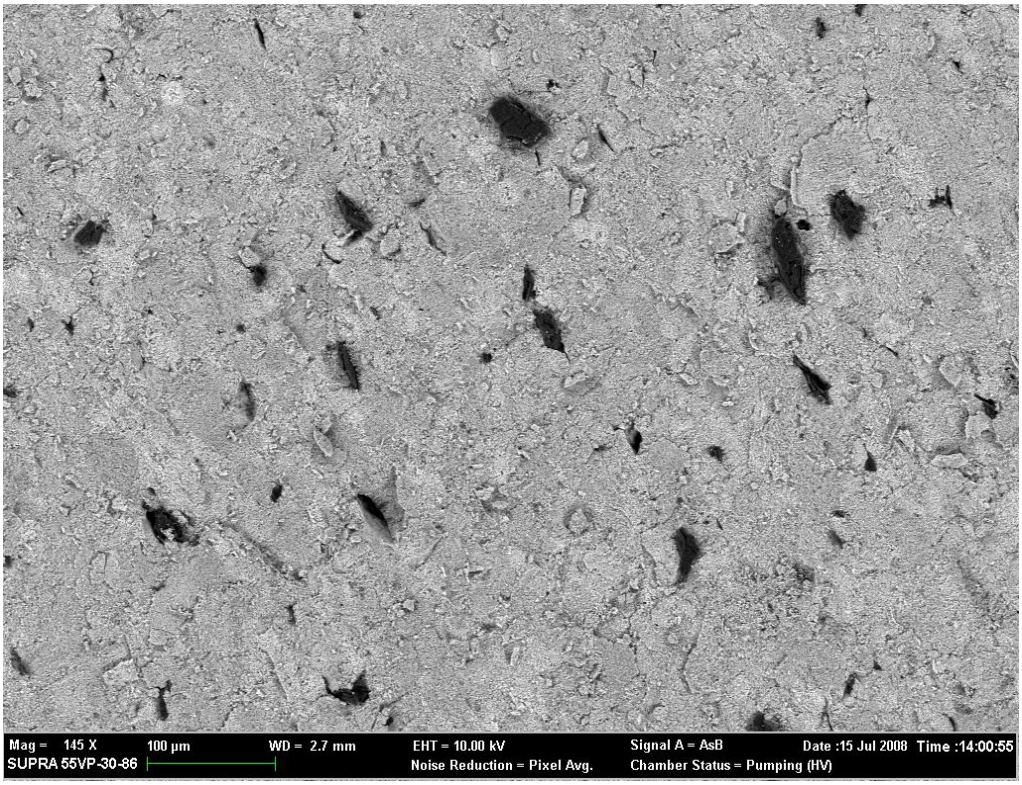


Figure 16 : Microphotograph of Activated Fresh Catalyst

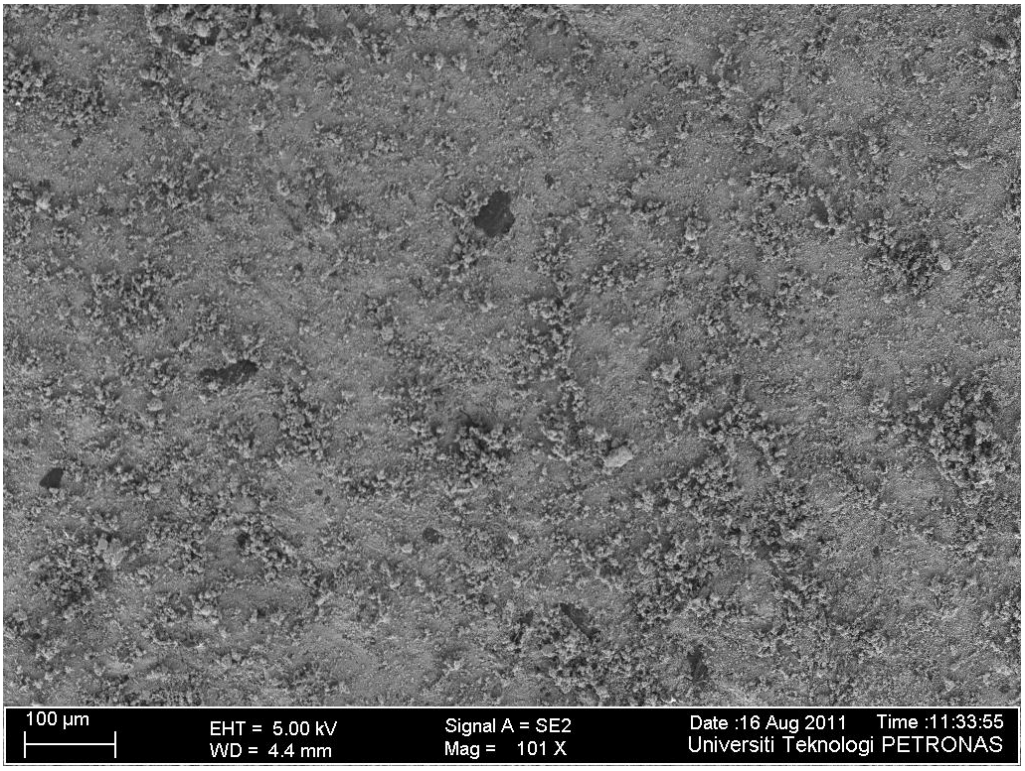


Figure 17 : Microphotograph of the 2-years spent catalyst from the Lurgi reactor (a)

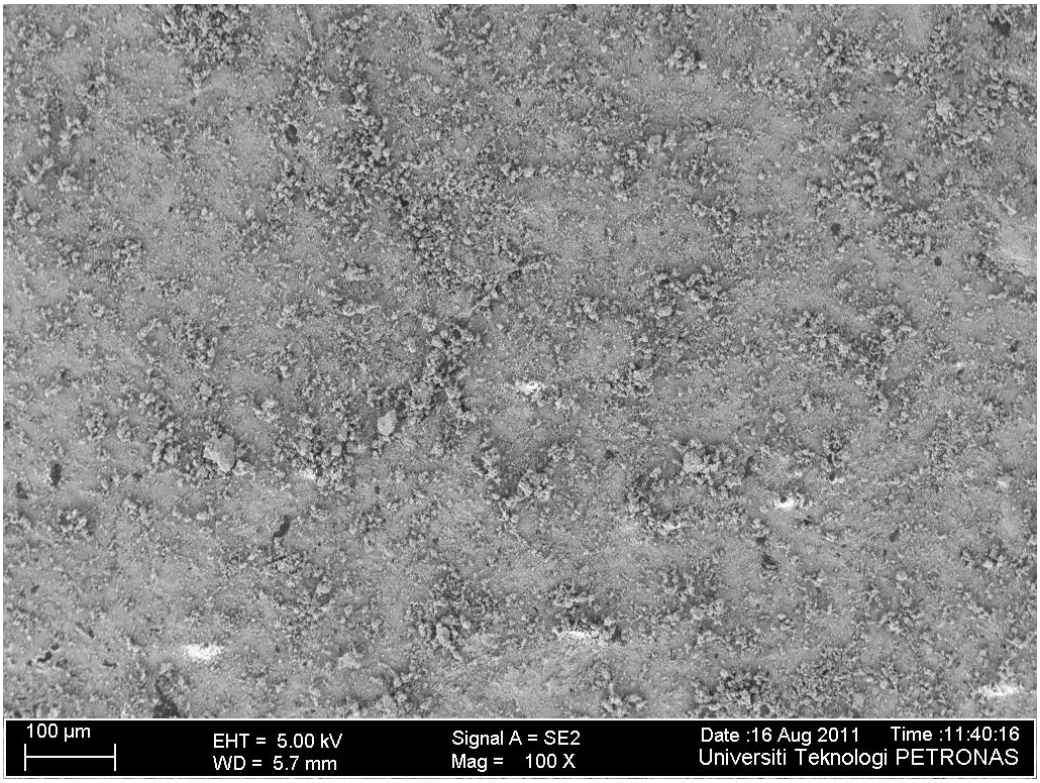


Figure 18 : Microphotograph of the 2-years spent catalyst from the Lurgi reactor (b)

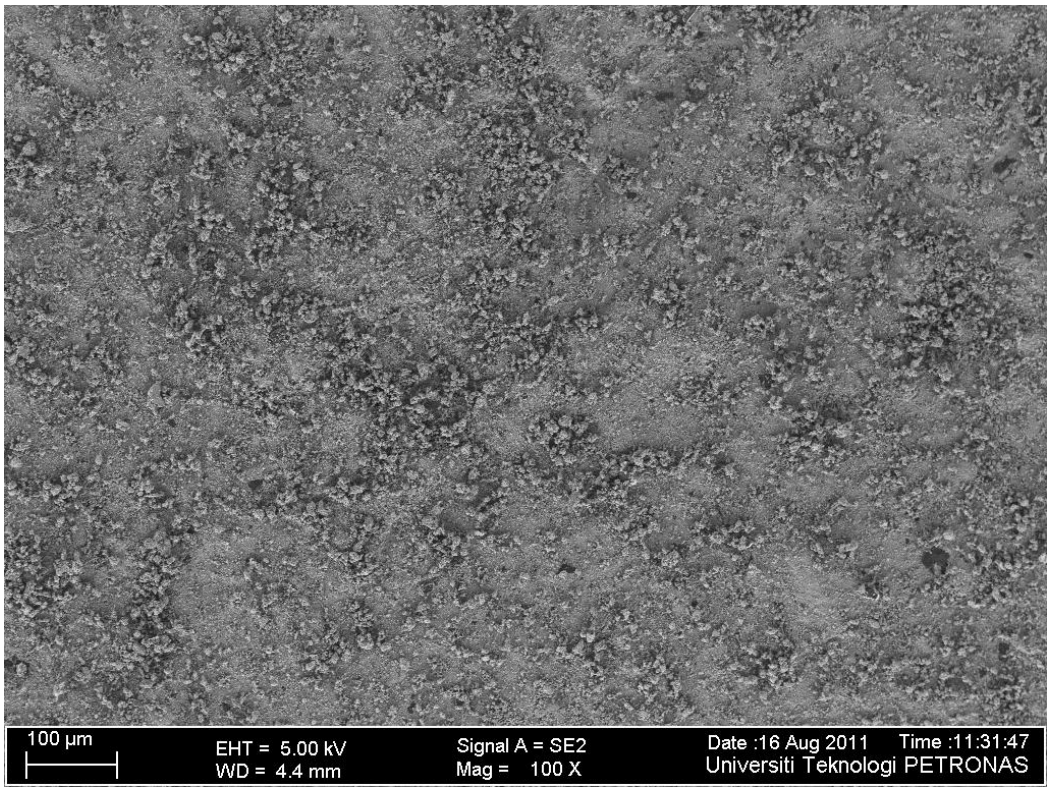


Figure 19 : Microphotograph of the 2-years spent catalyst from the Lurgi reactor (c)

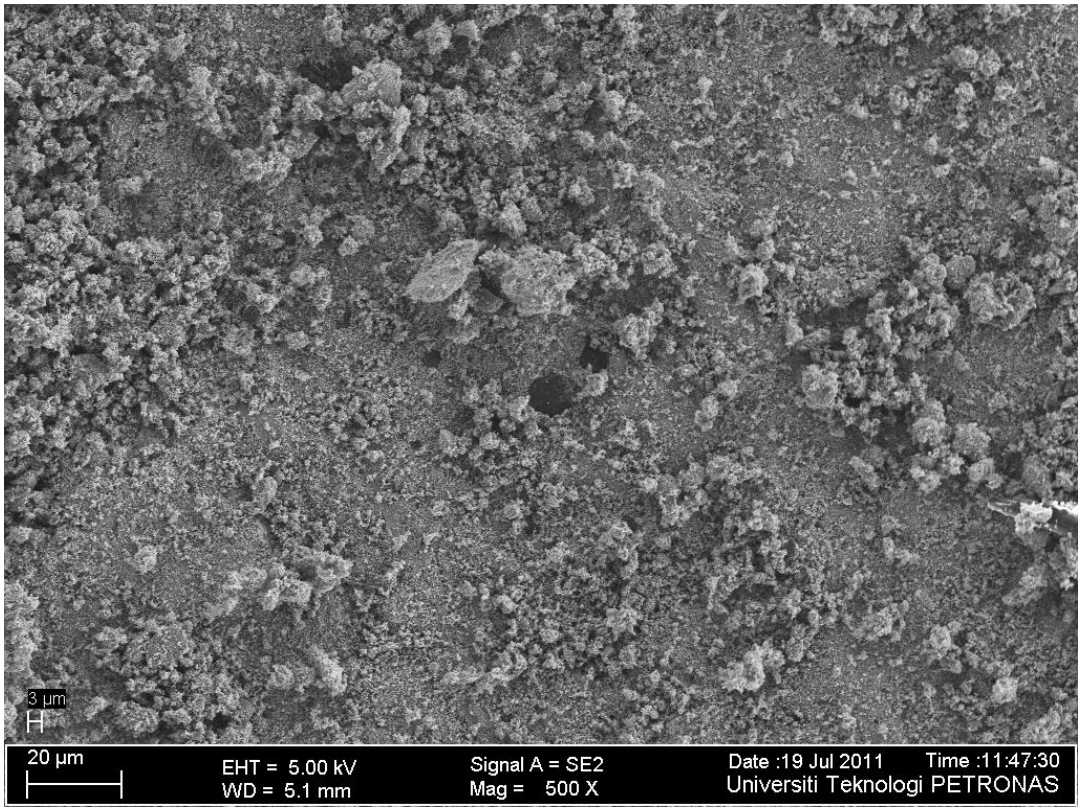


Figure 20 : Microphotograph of the 2-years spent catalyst from the Lurgi reactor (d)

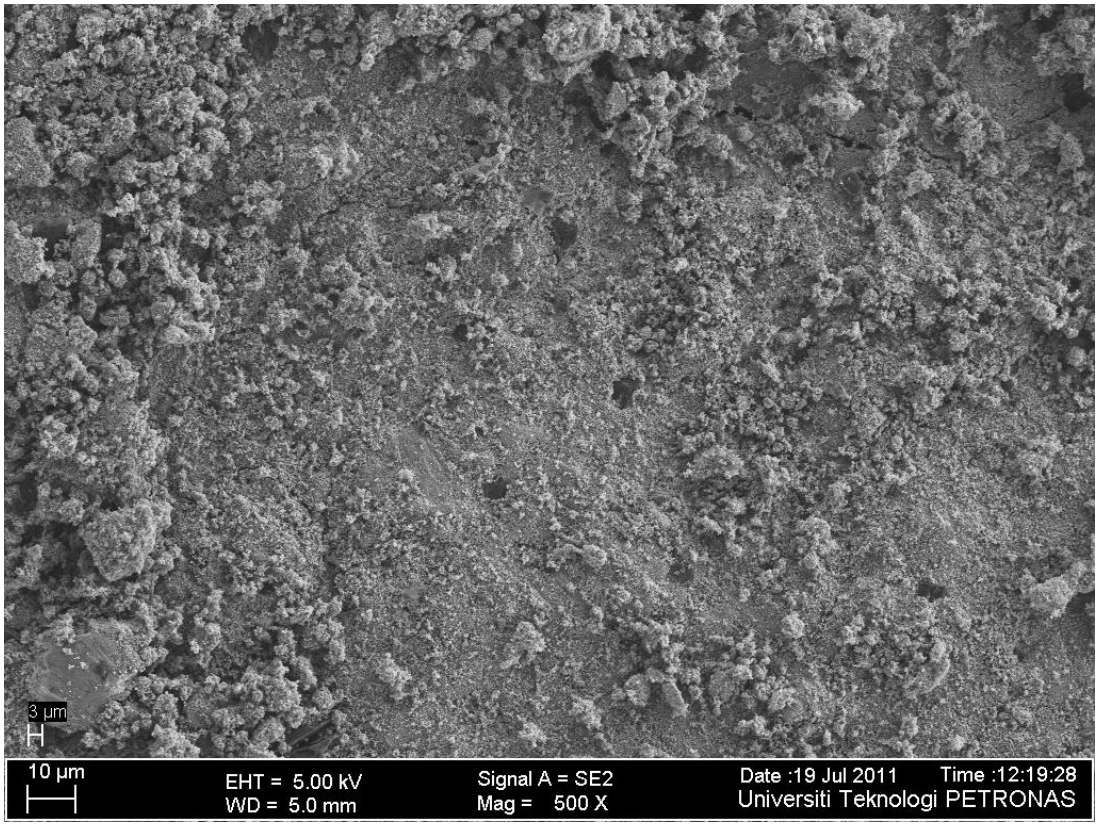


Figure 21 : Microphotograph of the 2-years spent catalyst from the Lurgi reactor (e)

As shown in Figure 16, the dark spots indicate that carbon element is existed the fresh catalyst surface. Based on literature review, the carbon acted as catalyst binding agent which inserted into the catalyst during pelletization process. [2]. Apart of that, the carbon is said to have high surface area, which supports the metal catalyst to disperse. [26]. However, the origin of coking on the surface of copper catalyst has not been established yet. This is because copper has no strong tendency to catalyse Fisher-Tropsch reactions, which usually give rise to carbonaceous deposits [4]. The most possible cause of deactivation by catalyst coking is involving CO by Boudouard reaction.

$$2CO(g) \rightarrow CO_2(g) + C(s)$$

However, this process usually occurs with insufficient hydrogen pressure and usually takes place at higher temperature than 250°C [3].

4.3.3 Elemental Analysis Using EDX

Dispersion of elements on the surface was analysed. By using this equipment, there are several elements detected; copper (Cu), zinc (Zn), oxygen (O), carbon (C) and Aluminium (Al). The elements dispersion on 2-years spent catalyst sample were compared with 3-years spent catalyst sample in order to detect changes on the surface morphology.

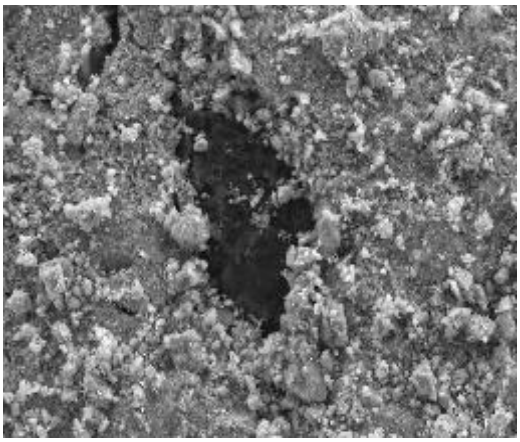


Figure 22 : Microphotograph of 3-years Spent Catalyst Surface

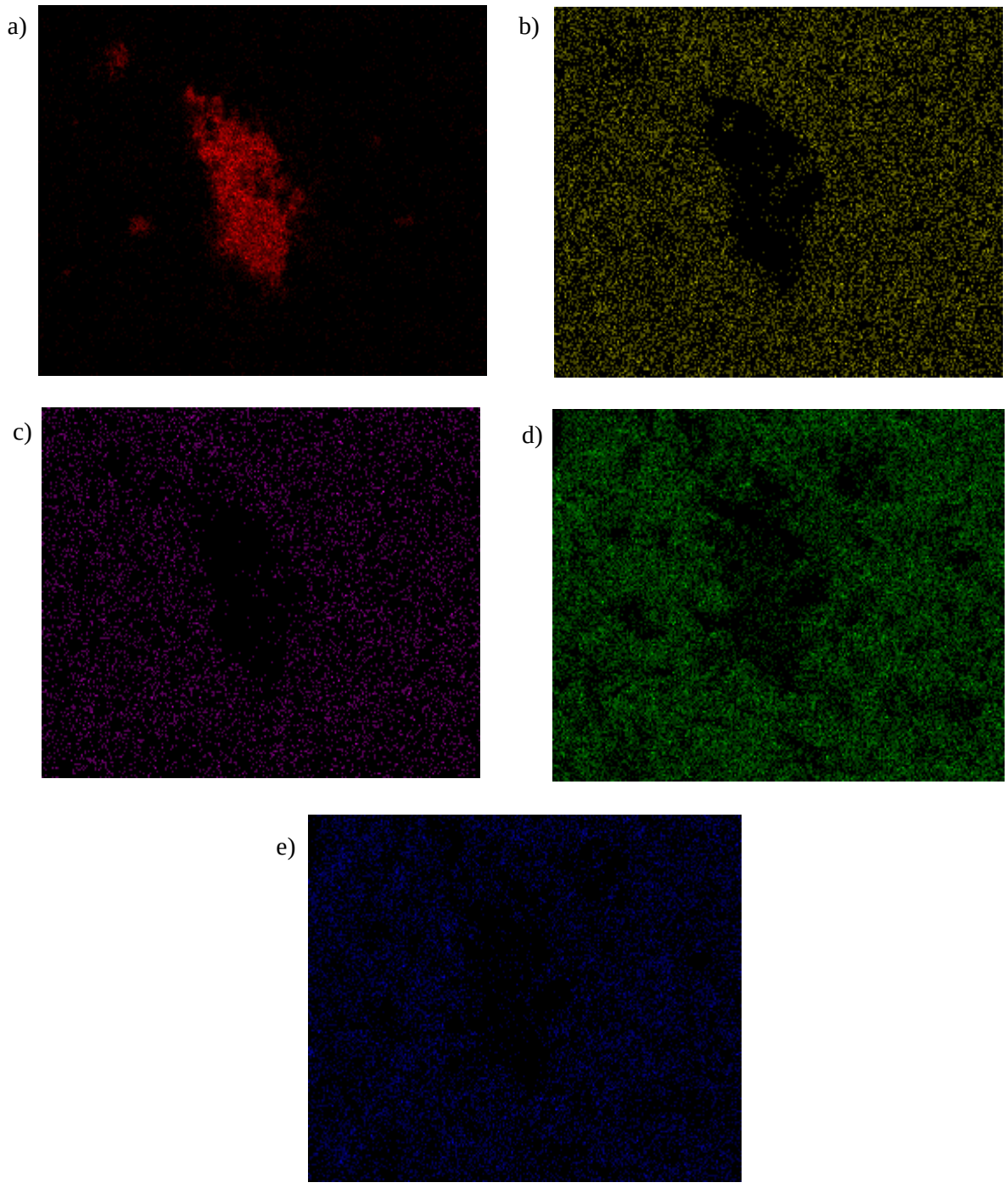
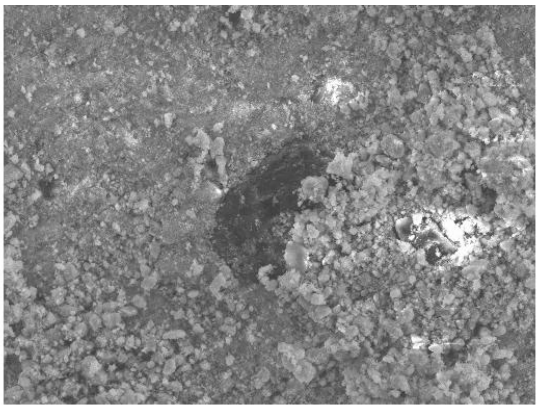


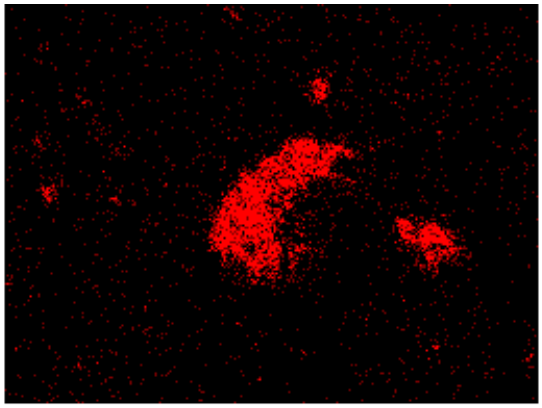
Figure 23 : Elemental Mapping of 3-years Spent Catalyst Surface a) Carbon b) Copper c) Zinc d) Oxygen e) Aluminium



Electron Image 1

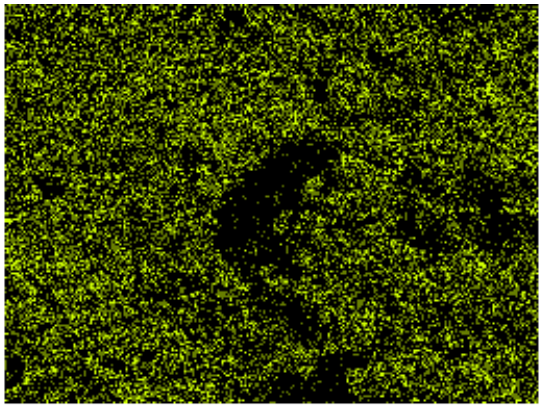
Figure 24 : Microphotograph of 2-years Spent Catalyst Surface

a)



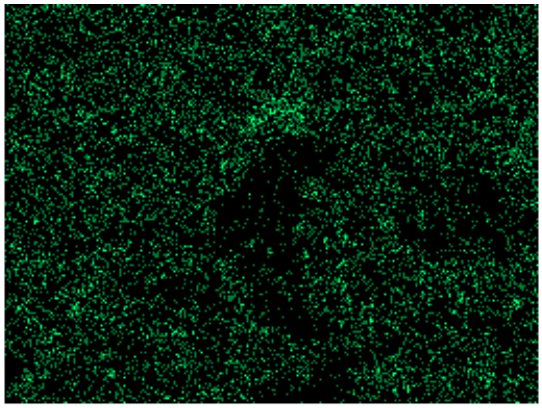
C Ka1_2

b)



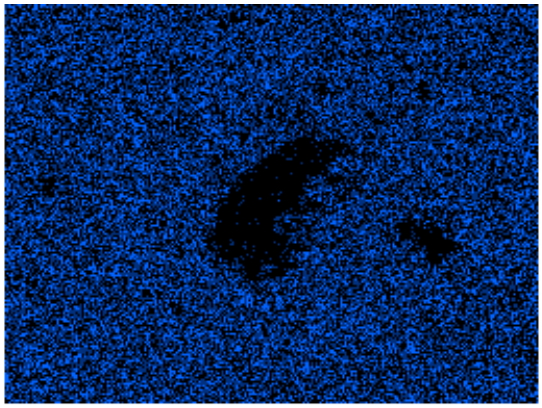
O Ka1

c)



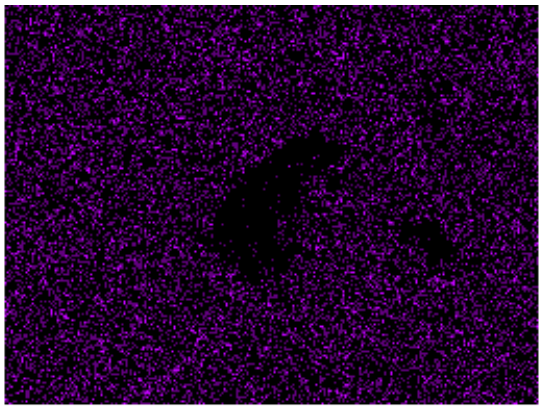
Al Ka1

d)



Cu Ka1

e)



Zn Ka1

Figure 25 : Elemental Mapping of 3-years Spent Catalyst Surface a) Carbon b) Oxygen c) Aluminium d) Copper e) Zinc

In this analysis, we put our focus on Cu and Zn elements because their combination builds the active site of this catalyst. Observing the dispersion of these elements, they are still well dispersed despite of being used in methanol production process. Therefore, we can assume that there is no influence of declining of catalyst activity in terms of dispersion as no sintering occurs on the surface.

On the other perspective, comparing the surface elemental composition on the spent and fresh catalysts, it was observed that there was no significant change.

Catalyst	**Composition of Fresh Sample (weight %)**	**Composition of 2-years Spent Catalyst Sample (weight %)**
Element		
Carbon	10.56	10.94
Oxygen	26.74	26.12
Aluminium	4.12	4.83
Copper	39.38	38.92
Zinc	20.08	19.18

Table 2 : Comparison of Compositions of the Catalyst Fresh and 2-Years Spent Catalyst Samples

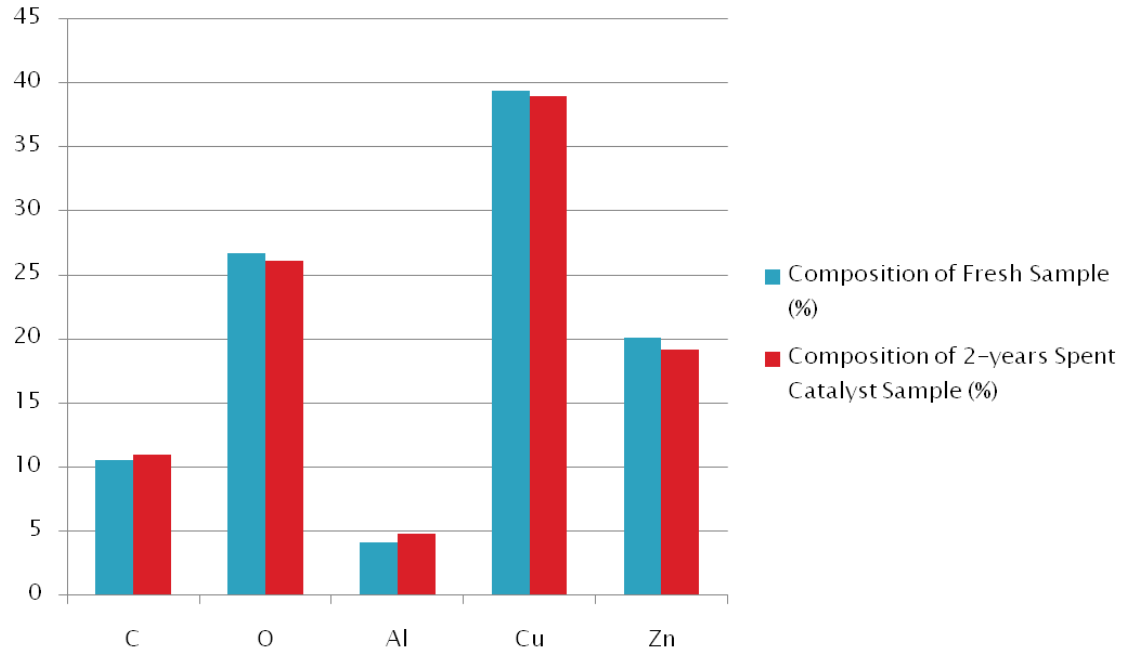


Figure 26 : Comparison of Compositions of the Catalyst Fresh and 2-Years Spent Catalyst Samples

4.4 Catalyst Deactivation Model

Based on results from the analytical methods (FESEM, EDX and XPS), a model of $Cu/ZnO/Al_2O_3$ catalyst deactivation on Lurgi methanol reactor output is proposed. The results shows poisoning process occurs on the catalyst surface which operates in this process, where sulphur compound (ZnS) takes place on the surface. [7]. As a result, the reactants, which is carbon monoxide (CO) and H_2 cannot access the active site which is the Cu/ZnO interface.

The basis of this model comes from the Strong Metal-Support Interaction (SMSI) theory between Cu and ZnO. This is because based on research, the combination of those metals shows great result in terms of increasing the methanol production rate. [30] Though copper seems to be the major source of the catalytic activity, Cu/ZnO catalysts showed better performance compared to Cu/Al_2O_3. The SMSI effect occurred due to strong reducing condition of the process, because of the presence of CO which has radical electron. This radical electron tend to be transferred to Zn metal, and partially reducing the ZnO component to be ZnO_{1-x}.

It was proposed [31] that the interface area between Cu and partially reduced ZnO is the important formation that creates active sites on the catalyst. This is because the Cu shows wetting behaviour on ZnO support. [2, 32] This wetting behaviour means that the Cu particles flattened and spread on the partially reduced ZnO metal as if they are mixed [33].

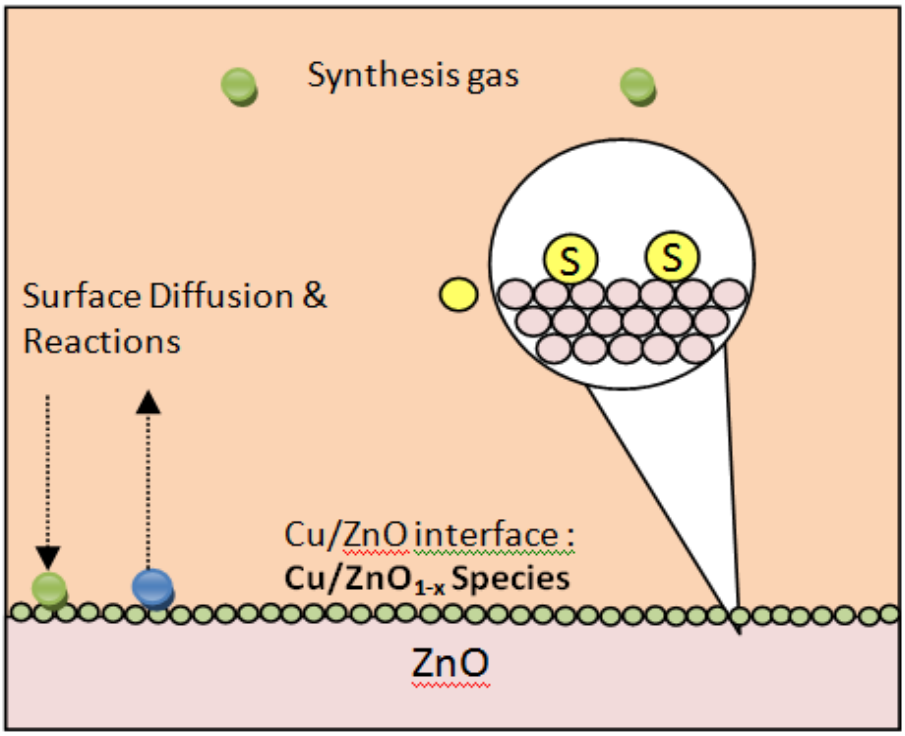


Figure 27 : $Cu/ZnO/Al_2O_3$ Catalyst Deactivation Model on Lurgi Reactor

As shown in the figure above, sulfur react with ZnO oxide because thermodynamically, the reaction between sulfur and ZnO is more favourable compare to Cu because enthalpy of reaction between sulfur and ZnO is higher.[4]

$$2Cu + H_2S \rightarrow Cu_2S + H_2;\ \Delta Ho = -59.4\ kJ\ mol^{-1}$$

$$ZnO + H_2S \rightarrow ZnS + H_2O;\ \Delta Ho = -76.7\ kJ\ mol^{-1}$$

The wetting behaviour of Cu create problem in this case because even though the sulfur molecules react with ZnO, due to flat orientation of Cu on ZnO, the existence of sulfur will distort the surface of the catalyst. This phenomenon causes the Cu crystallites to turn around and exposing the inert facets of the crystal outward. Based on literature review, only Cu(111)

face shows catalytic activity toward the reaction, while other facets, Cu(110) and Cu(211) not. [2, 28].

CHAPTER 5

CONCLUSION

The main objective of this project is to study the surface changes on the $Cu/ZnO/Al_2O_3$ which lead to deactivation of this catalyst. The origin has been revealed by using high-technology chemical analysis instruments like Field Emission Scanning Electron Microscopy, elements analysis using Energy X-ray Dispersive Analysis and chemical compound analysis by using X-ray Photoelectron Spectroscopy.

Based on the findings of the surface analysis, the poisoning of the catalyst occurred because of impurities that exist within the process stream; the sulphur. The impurities most likely came from the synthesis gas process which suggested that the performance of the catalyst influenced by the natural gas feed at synthesis gas process. Meanwhile, the dispersion of Cu and ZnO not affected by the process condition as no sintering occurred. This is because the melting temperature of both component is 1080°C and 1975°C respectively. This data indicates that they have Tammann temperature is higher than the process condition, 250°C. The carbon is existed since the catalyst is manufactured by the company, where the carbon acted as binding agent in pelletization process. The data obtained from these analytical methods lead us to proposed a deactivation model specifically for Lurgi reactor process condition.

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APPENDIX A

XPS Spectrums

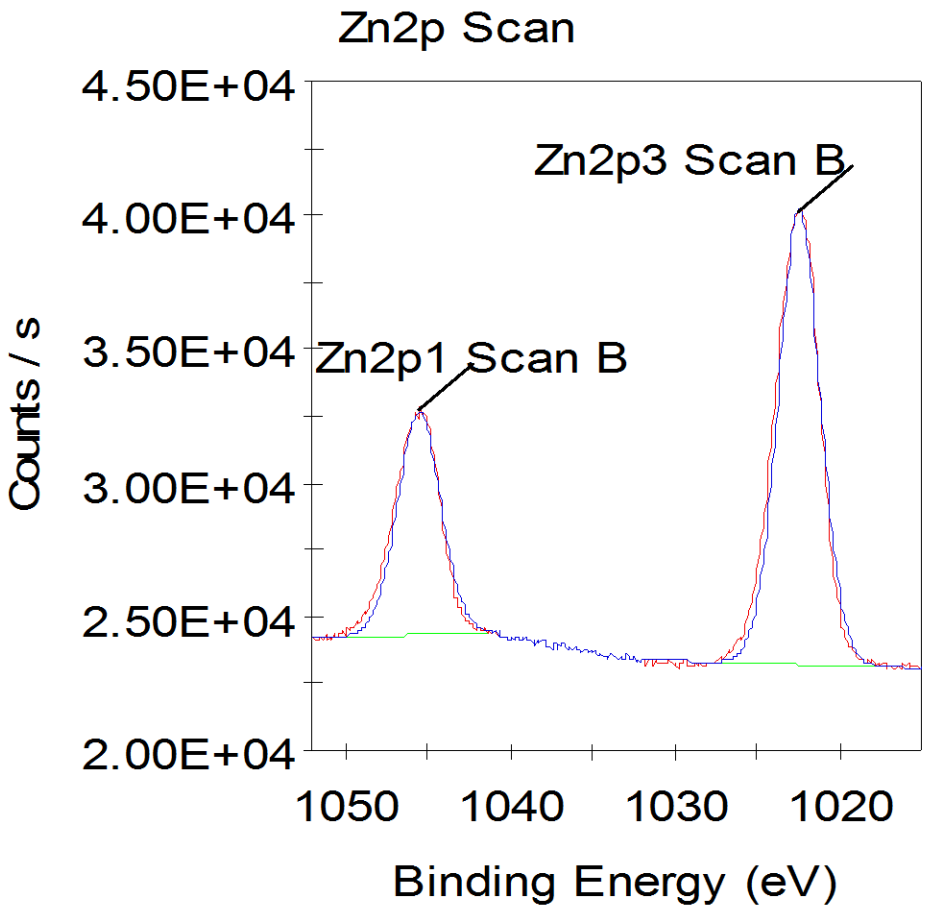


Figure A-1 : Chemical State Spectrums of Zn (Sample 1)

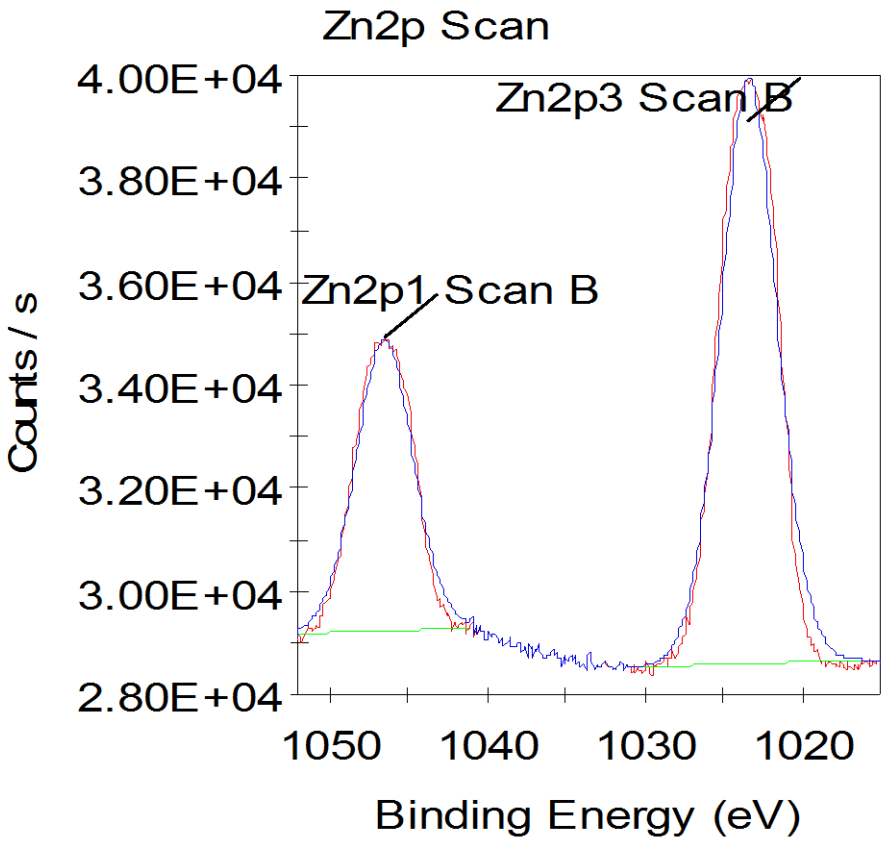


Figure A-2 : Chemical State Spectrums of Zn (Sample 2)

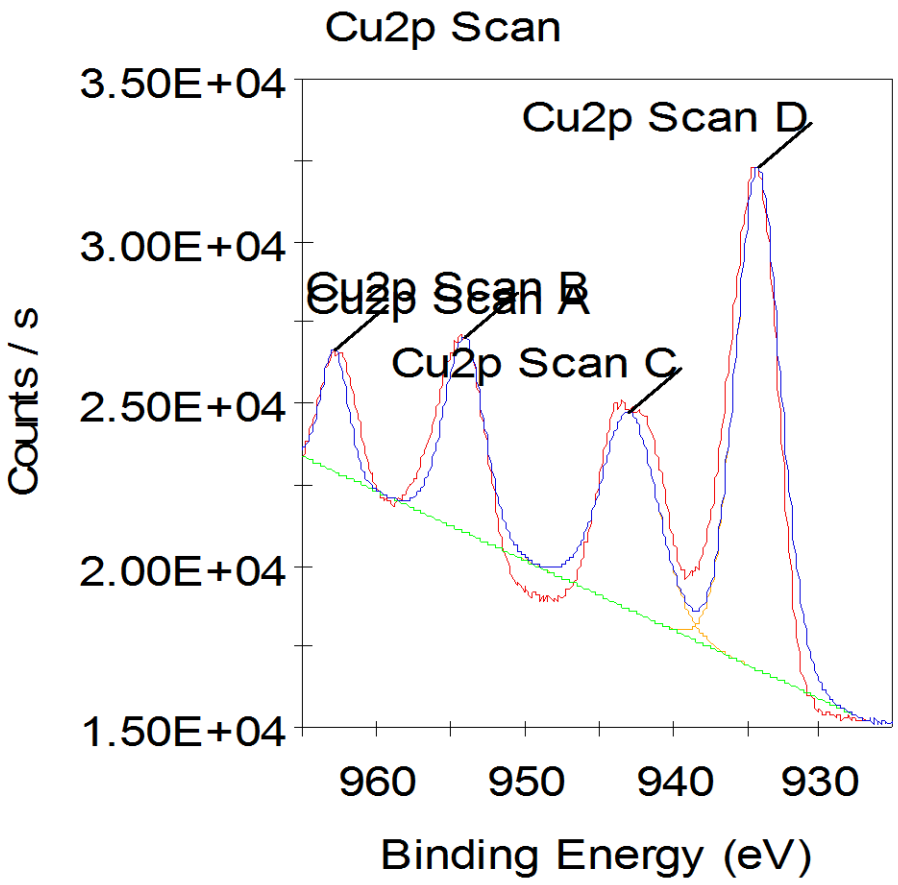


Figure A-3 : Chemical State Spectrums of Cu (Sample 1)

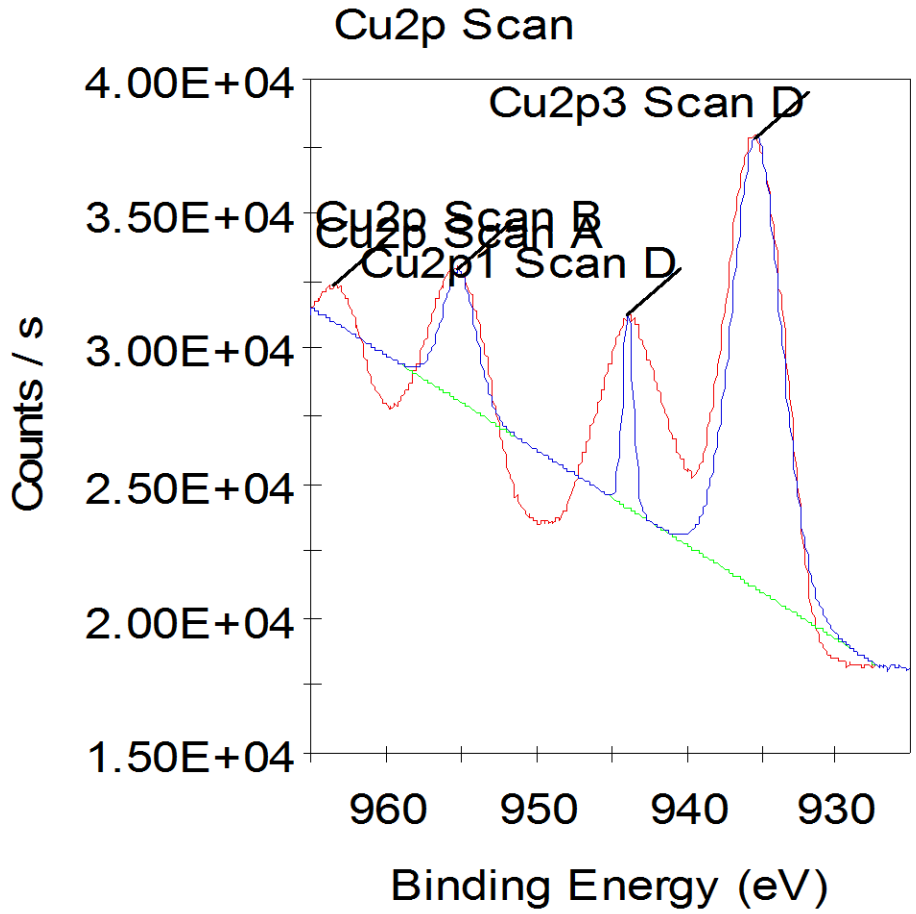
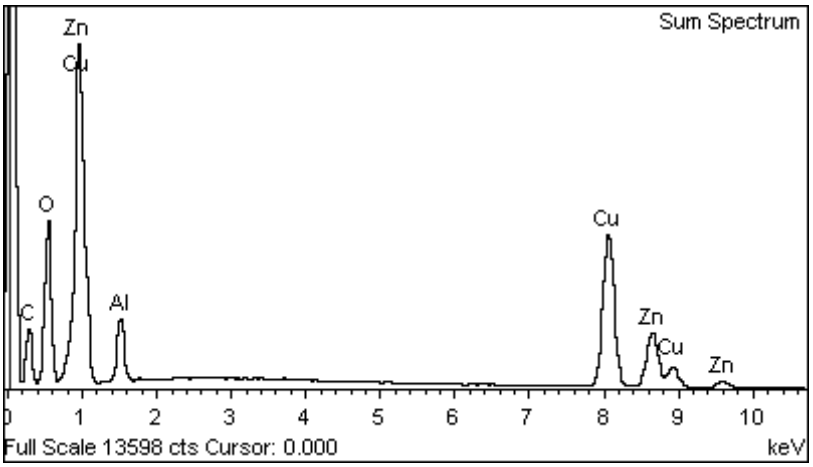


Figure A-4 : Chemical State Spectrums of Cu (Sample 2)

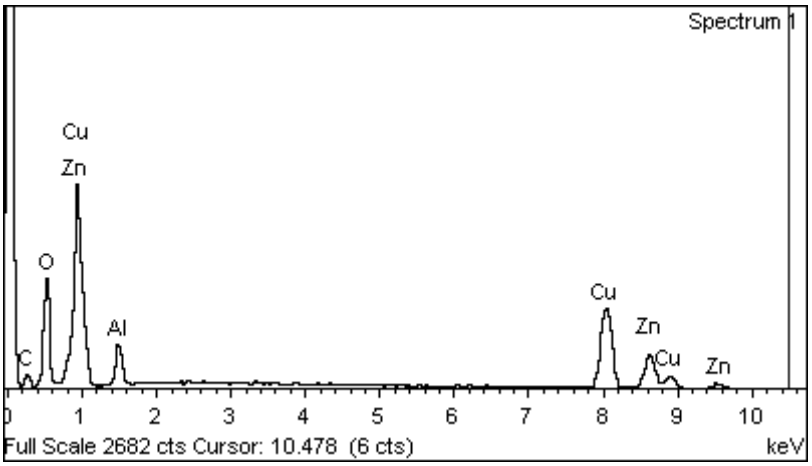
APPENDIX B

EDX Analysis



Element	Weight%	Atomic%
C K	22.94	44.63
O K	23.48	34.30
Al K	3.06	2.65
Cu K	34.76	12.79
Zn K	15.76	5.63
Totals	100.00	

Figure B-1 : Chemical Elemental Analysis of 2-Years Spent Catalyst (Sample 1)



Element	Weight%	Atomic%
C K	13.02	29.36
O K	24.70	41.83
Al K	4.30	4.32
Cu K	39.03	16.64
Zn K	18.95	7.85
Totals	100.00	

Figure B-2 : Chemical Elemental Analysis of 2-Years Spent Catalyst (Sample 2)